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THE RAMAN SPECTRA OF 1, 3-DIBROMOPROPANE AND 1, 2, 3-TRICHLOROPROPANE IN THE SOLID STATE*

By B. M. BISHUI

Optics Department, Indian Association for the Cultivation of Science, Calcutta 32

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Plate VII

ABSTRACT. The Raman spetra of 1, 3-dibromopropane and 1, 2, 3 trichloropropane have been investigated in the solid state at −180°C. It has been observed that in the first case some of the Raman lines disappear with solidification, while in the case of the second liquid all the prominent Raman lines persist even when the liquid is solidified and cooled to −180°C. It is pointed out that although the results reported by previous workers indicate the presenee of two rotational isomers even in the case of normal paraffins in the liquid state and disappearance of one of the rotational isomers with the solidification of the liquids, the results observed in the case of 1, 2, 3-trichloropropane do not indicate such disappearance of one of the isomers with the solidification of the liquid. It is pointed out that the presence of extra lines cannot be due to presence of two isomeric molecules in the liquid state of this compound

INTRODUCTION

The Raman spectra of many substituted paraffins have been studied previously by several workers at different temperatures and in different states, and results have been interpreted on the assumption that the liquid state contains two isomers, one of which disappears in the solid state. Even in the case of some monosubstituted propanes, *e g.*, propyl halides also, such a disappearance of some of the Raman lines has been observed previously (Mizushima *et al*, 1940 ; Bishui, 1948*a*).

In order to verify whether disubstituted and trisubstituted propanes also behave in the same way as monosubstituted propane, the Raman spectra of 1, 3-dibromopropane and 1, 2, 3-trichloropropane have been studied in the liquid and solid states in the present investigation.

EXPERIMENTAL

The liquids 1, 3-dibromopropane and 1, 2, 3-trichloropropane were procured from B. D. H. (London) and Fisher Scientific Company (New York) respectively and redistilled in vacuum. The apparatus used in the present investigation for the study of the Raman spectra of the substances in the solid state at low temperatures was the same as described earlier (Bishui, 1948*b*). The liquid was put in a Pyrex glass tube held in a vertical position in the transparent liquid oxygen container of Pyrex glass. The liquid oxygen was transferred to the transparent Dewar vessel by an arrangement with Cenco

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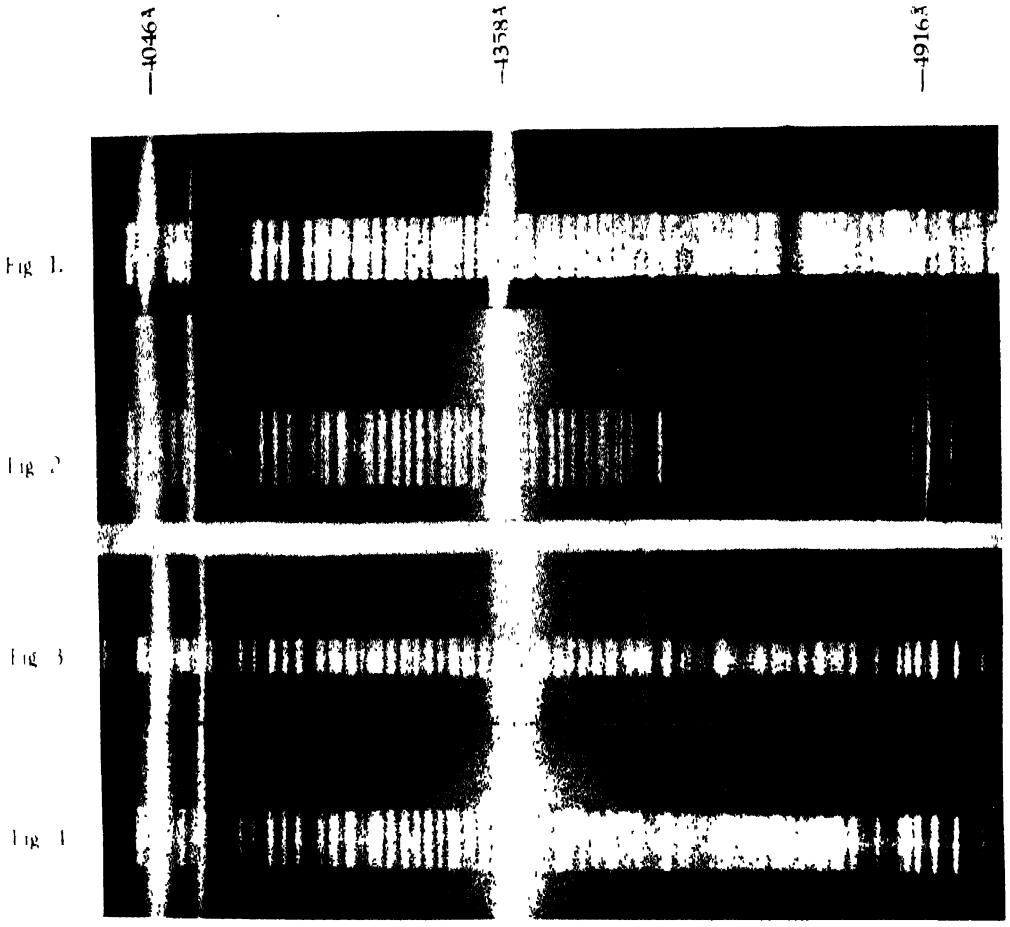

Raman spectra

Fig. 1. 1, 3-Dibromopropane at 30 C.

Fig. 2 „ „ „ 180 C.

Fig. 3. 1, 2, 3- Trichloropropane at 30°C.

Fig. 4. —180 C.

Hyvac pump so that the level of the liquid oxygen was initially much below the bottom of the container containing the liquid ,which was thus cooled very slowly. Consequently, the process of solidification was very slow. The frozen mass thus produced was transparent.

A Fuess glass spectrograph having a dispersion of about 14 Å per mm in the region of 4046 Å was used. The transprent solid mass was illuminated by light from two vertical mercury arcs condensed by two glass condensers placed on opposite sides of the container. Cobalt glass filters were placed in the path of the incident rays to cut off continuous background in the blue-green region of the spectrum. The Raman spectra of the liquids at room temperature were photographed in the usual way.

RESULTS AND DISCUSSION

The spectrograms for the liquid and the solid states of the two substances are reproduced in Plate VII. The frequency-shifts are given in Tables I and II in which the data for liquid state reported by previous workors are also included for comparison. The visually estimated intensities of the lines are given in the parentheses.

TABLE I

1, 3-Dibromopropane $BrCH_2.CH_2.CH_2Br$

Liquid at 30°C		Solid at −180°C
Kohlrausch and Ypsilanti (1936)	Present author	Present author
187(6)	188(3) e, k	———
211(2b)	210(2b) e, k	230(0) e, k
313(2)	315(1b) e, k	
378(3)	374(3) e, k	— — —
421(7)	428(4) e, k	426(1) e, k
550(10)	552(5) e, k	552(2) e, k
562(10)	564(5) e, k	— — —
589(15)	589(6) e, k	594(3) e, k
648(9)	654(5) e, k	———
696(4)	696(2) e, k	— — —
757(3)	768(1b) e, k	———
855(4)	861(1b) e, k	861(0) e, k
943(3)	953(1) e, k	
998(1)	998(0) e, k	
1046(2)		
1117(3)	1240(3) e, k	———
1170(0)	1295(3) e, k	———
1236(8b)	1353(1) e, k	———
1291(4)	1417(2) e	
1340(1)	1438(4) e, k	— — —
1417(5)	2830(1) k	
1437(6)	2858(2) k	
2840(2)	2909(5) e, k	2909(4) e, k
2908(7)	2930(4b) e, k	2930(3) e, k
2966(10)	2972(6) e, k	2972(4) e, k
		2998(2)
3016(3)	3008(4) e, k	3012(2) e, k

TABLE II

1, 2, 3-Trichloropropane Cl. H_2C. CH (Cl). CH_2Cl

Liquid at 30°C		Solid at −180°C
Kohlrausch and Ypsilanti (1936)	Present author	Present author
	88(2) e, k	94(2) e, k
	138(0) e	
188(0)	190(0) e	
227(0)	237(0) e	
288(5)	294(6) e, k	292(2) e, k
356(4)	357(3) e, k	357(0) e, k
381(1)	387(2) e, k	———
412(1)	418(2) e, k	———
519(3)	524(1) e, k	524(1) e, k
628(1)	637(0) e, k	632(1) e, k
660(6)	667(6) e, k	664(3) e, k
716(4)	718(5) e, k	718(3) e, k
746(8)	752(6b) e, k	752(4) e, k
863(3)	872(3) e, k	872(c) e, k
906(0)	905(0) e, k	———
931(0)	934(0) e, k	———
990(½)	995(2) e, k	1005(1) e, k
1090(½)	1094(4b) e, k	1094(1) e, k
1198(2)	1190(0) e, k	———
1283(3)	1285(2b) e, k	1280(0) e, k
1338(1)	1347(1b) e, k	1347(0) e, k
1432(3b)	1438(5b) e, k	1440(1) e, k
2860(2) f	2962(8b) e, k	2966(2) e, k
2960(10b)	3015(4b) e, k	3024(2) e, k
3008(6)		

DISCUSSION

The results given in Table I show that in the case of 1, 3-dibromopropane in the liquid state all the lines observed by Kohlrausch and Ypsilanti (1936) are observed in the present investigation excepting the lines 1046, 1117 and 1170 cm^{-1}. The first of the three lines was found to be definitely absent and the other two supposed to be excited by 4046 Å are actually the antistokes frequencies 650 and 597 cm^{-1} excited by the 4358 Å line. The corresponding lines excited by the 4358 Å lines could not be detected. So the liquid studied was the same as that studied by Kohlrausch and Ypsilanti (1936), It is observed from Table I that the strong lines 374, 564, 654 and 1438 cm^{-1} disappear with the solidification of the liquid. In the case of *n*-propyl bromide only one of the lines due to C-Br valence oscillation disappeared with solidification (Bishui, 1948*a*) while in the present case the two lines 564 and 654 cm^{-1} probably due to such oscillations disappear when the liquid is frozen. Similar results observed in the case of *n*-propyl chloride were explained by Mizushima, Morino and Nakamura (1940) on the assumption that the liquid contains two types of isomeric molecules one

of which disappears with solidification. If similar hypothesis is applied in the present case it is found that the disappearance of the strong line 1438 cm^{-1} due to C-H deformation oscillation cannot be explained.

It is observed that the lines due to C-H valence oscillation b come sharper with solidification of the liquid and the line 3008 cm^{-1} splits up into two lines at 2998 and 3012 cm^{-1} respectively. If it is assumed that the two lines 564 and 654 cm^{-1} are due to C-Br vibration in one of the isomeric forms of the molecule the other two lines 552 and 594 cm^{-1} are the corresponding lines due to the other form. If these frequencies for the two forms be so different from each other the frequencies of C-H oscillations of the two forms also ought to have been slightly different from each other, but actually all the prominent lines due to C-H valence oscillation persist in the case of the solid state.

The results given in Table II show that all the prominent lines observed in the case of 1, 2, 3-trichloropropane persist when the liquid is solidified at $-180°C$. As the the three chlorine atoms are attached to three different carbon atoms, different isomeric molecules can be formed by rotation about the C-C bond. Even in the case of *n*-paraffins Sheppard and Szasz (1949) have observed that some of the Raman lines disappear with the freezing of the liquid and they have explained the results on the assumption that one of the two isomeric forms disapears in the solid state. The persistence of all the lines in the case of solid 1, 2, 3-trichloropropane thus shows that the presence of two types of isomers in the liquid state of this compound cannot be assumed to explain the presence of any extra lines in the Raman spectrum of this substance. There are 17 lines of frequency-shifts below 1100 cm^{-1} excluding the line 88 cm^{-1} in the Raman spectrum of this liquid, while in the case of 1, 3-dibromopropane there are 14 such lines. The number of heavy atoms in the former molecule is six while in the latter case it is five. So the extra three lines in the former case is due to the additional chlorine atom attached to the central carbon atom. The 14 lines in the case of 1, 3-dibromopropane, however, are not due to a single molecule, as some of them disappear when the liquid is frozen. Hence in the case of 1, 2, 3-trichloropropane also these seventeen lines cannot be due to a single molecule. Since all of them persist in the case of the solid they cannot be due to two isomeric forms of the molecule. The only other alternative explanation which can be offered is that in this particular case the presence of three chlorine atoms in molecule makes the molecule strongly polar and the molecules are strongly associated both in the liquid and solid states. This hypothesis can be tested only by investigating the Raman spectrum of the substance in the vapour state, but as it is very difficult te record the feeble Raman lines in the case of vapour no attempt has been made to verify the hypothesis.

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